EFFECT OF PROMOTERS (Mn, Zn and ZrO_2) ON THE CHARACTERIZATION OF SBA-15 SUPPORTED COBALT CATALYST FOR FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Fischer–Tropsch synthesis (FTS) is a part of gas-to-liquids (GTL) technology, which produces synthetic liquid hydrocarbons from natural gas. Recently the production of clean fuels and particularly of synthetic diesel by means of the FTS process has aroused renewed interest in both industrial and academic field. This process was shown to be catalyzed by certain transition metals, such as Co which present the highest activity. This research work is about the synthesis of SBA-15 and preparation of catalyst with different promoter Zr, Zn, Mn – Co based supported by SBA-15 by wet impregnation catalysts and characterizes all sampling. All materials were characterized by several physico-chemical techniques such as TGA, SEM and FTIR. The catalytic and characterization results show a great influence of mesoporous support porosity on the structure, reducibility and FTS catalytic behavior of cobalt oxide species supported over these ordered materials. After modification of SBA-15 by Co with different loading, the particles found to be attached closely with each other. The SEM picture shows a large number of SBA-15 particles attaching closely with one another. So this will make catalyst more efficient and effective during FT process. Then, using FTIR, the functional groups will be observed with certain wavelength in the samples such as cobalt oxides, Si-O-Si, Si-CH_3, zinc oxide, OH band, Si-C, and others. Besides that, the identification of metal inside SBA-15 was determined by comparing the pure SBA-15 with the incorporated metal on SBA-15. For this research, the characterization of the catalyst by selecting Zn as promoter have quiet similar characterization with noble metal that already investigate.

ABSTRAK

Fischer-Tropsch sintesis (FTS) adalah sebahagian daripada proses penukaran gas kepada cecair (GTL), yang menghasilkan cecair hidrokarbon sintetik dari gas asli. Baru-baru ini pengeluaran bahan api bersih terutamanya diesel sintetik melalui proses FTS telah menimbulkan minat dalam bidang industri dan akademik. Proses yang telah dimangkinkan oleh logam peralihan yang tertentu, yang menunjukkan aktiviti yang tinggi. Penyelidikan tentang sintesis SBA-15 dan penyediaan pemangkin dengan unsur penggalak yang berbeza, Zn, Mn - Co berasaskan/disokong oleh SBA-15 melalui kaedah impregnasi yang sedikit basah.Sifat-sifat mangkin di percirikan dengan menggunakan teknik fizik-kimia seperti TGA, SEM dan FTIR. Hasil keputusan pencirian menunjukkan liang meso mempunyai pengaruh yang besar pada struktur dan tingkah laku sebagai pemangkin spesis oksida kobalt disokong ke atas bahan-bahan ini yang diperintahkan. Selepas pengubahsuaian SBA-15 oleh bersama dengan unsur penggalak yang berbeza, zarah didapati rapat antara satu sama lain. Gambar SEM menunjukkan sebilangan besar SBA-15 menunjukkan zarah rapat antara satu sama lain. Jadi ini akan menjadikan pemangkin yang lebih cekap dan berkesan semasa proses FT. Kemudian, dengan menggunakan FTIR, kumpulan berfungsi akan diperhatikan dengan panjang gelombang tertentu dalam sampel seperti oksida kobalt, Si-O-Si, Si-CH3, zink oksida, OH band, Si-C, dan lain-lain. Selain itu, pengenalan logam di dalam SBA-15 telah ditentukan dengan membandingkan SBA-15 yang asli dengan SBA-15 yang telah dimpregnasikan dengan logam. Untuk kajian ini, didapati ciri-ciri mangkin dengan pemilihan Zn sebagai unsur penggalak mempunyai ciri-ciriyang sama dengan logam aktif yang telah digunakan sebelum ini.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

FTIR	Fourier Transform infrared Spectra
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
FT	Fisher Tropsch
WGS	Water Gas Shift
TEM	Transmission Electron Microscopy
SCR	Selective Catalytic Reduction
Zn	Zinc
Co	Cobalt
Mn	Mangan
CoO	Cobalt Oxide
GTL	Gas to liquid
Al_2O_3	Alumina

CHAPTER 1

INTRODUCTION

1.1 Background of study

Nowadays, a large fraction of chemical, refinery and pollution control process involve catalyst. For example In 1993 the worldwide catalyst usage was $8.7 billion , comprising $3.1 billion for chemical,$3 billion for environmental application, $1.8 billion for petroleum refining, and $0.8 billion for industrial biocatalyst(schilling and Thayer.,1994) . So we can see that how much industry spent money for the catalyst. Fischer Tropsch process also involves more cost. The Figure below show the overall Fischer-Tropsch process.

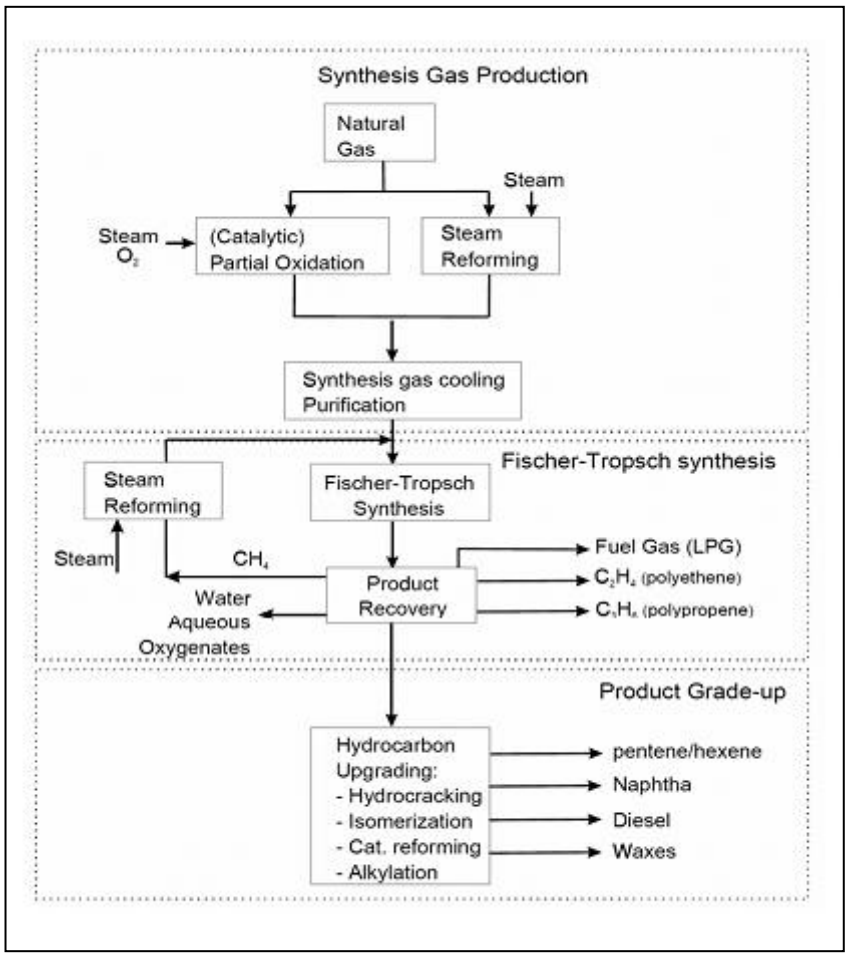

Figure 1.1: Block diagram of the overall Fischer-Tropsch process

Configuration

Fischer-Tropsch(FT) synthesis is a part of gas to liquid(GTL) technology, which is a chemical process that produces high hydrocarbons chain from syngas (carbon monoxide &hydrogen). Natural gas can be converted to carbon monoxide and hydrogen (synthesis gas) via existing or newly developed processes such as steam reforming, carbon dioxide reforming, partial oxidation and catalytic partial oxidation, followed by the Fischer–Tropsch synthesis reactionin which "–CH2" represents a product consisting mainly of paraffinic hydrocarbons of variable chain length (Sie, 1999). Fischer-Tropsch synthesis is catalyzed by transition metal such as Co, Fe, and Ru.Among them, cobalt based catalyst are preferred for their high activity compared to Fe catalyst. Besides that, cobalt based catalyst produce high

yield of long chain paraffin, low activity for the competing water gas shift reaction and lower price than metal like Ru(Lira et al.,2008)Usually, for catalyst support silica-based mesoporous material such as MCM-41 and SBA-15 are the common catalyst support using in GTL plant. The most common Fischer-Tropsch catalysts are group VIII metals (Co & Fe). Iron catalysts are commonly used, because of their low costs in comparison to other active metals. Iron catalysts have a high water gas shift activity, high selectivity to olefins and appear to be stable when synthesis gas with a high H2/CO ratio is converted. Table below show the price ratio of the metal.

Table 1.1: Relative prices of metals

Metal	Price ratio
Iron	1
Cobalt	230
Nickel	250
Ruthenium	31,000
Rhodium	570,000

Cobalt catalysts give the highest yields and longest life-time and produce predominantly linear alkanes. A cobalt catalyst on kieselguhr became the standard catalyst for commercial purposes in the Second World War in Germany. Disadvantages are the high costs of cobalt and low water gas shift activity. Therefore, cobalt catalysts are viable for natural-gas based Fischer-Tropsch processes for the production of middle distillates and high-molecular weight products. Cobalt catalysts are resulting in a higher productivity at a high synthesis gas conversion. In short, it can be said that Fe catalysts are more versatile yet more vulnerable to being damaged and are cheaper than cobalt catalysts. From the chemical standpoint, the Fe structure is simpler and is more easily enhanced which in turn increases its selectivity and life length.

The reactions of the FT synthesis on iron catalysts can be simplified as a combination of the

$$CO + (1 + m/2n)H_2 \rightarrow 1/nC_nH_m + H_2O \quad (FT)\ -\Delta H_{FT} = 165\ \text{kJ/mol}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (WGS)\ -\Delta H_{WGS} = 41.3\ \text{kJ/mol}$$

Where n is the average carbon number and m is the average number of hydrogen atoms of the hydrocarbon products. Water is a primary product of the FT reaction, and CO_2 can be produced by the WGS reaction. The water gas shift (WGS) activity can be high over iron catalysts and is negligible over cobalt catalysts.

The Fischer-Tropsch product spectrum consists of a complex multi component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffin's and -olefin. The hydrocarbon synthesis is catalyzed by metals such as cobalt, iron. This process operation conditions are: T: 300~350^{o}C & P:20~25 bar. Cobalt is used commercially these days for this process at a temperature of 180 to 240 °C and at 20 to 60 bar pressure. Table 1.2 below show main reactions involve in Fisccher-Tropsch synthesis.

Table 1.2: Major overall reactions in the Fisccher-Tropsch synthesis

Main reactions	
1. Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
2. Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
3. Water gas shift reaction	$CO + H_2O \rightleftarrows CO_2 + H_2$

The siliceous SBA-15 possesses big tubular channels ranging from 3-30 nm diameters. It also possesses the greater thickness of the pore wall and the hydrothermal stability is much higher than MCM-41 (Anunziata et al., 2007) and

large surface area (600 -1000 m^2/g) allowing for the dispersion of a large number of catalytically active species (Haifeng et al ., 2008). There was an obvious pore size effect on product selectivity probably due to the pores being sufficiently large for the reaction easily to proceed. Thus, SBA-15 is the better choice to be introduced as the support.

In order to gain access to the active sites, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spillover from the promoter surface (Knifton and Lin., 1982). Promoter is the site of keeping activity at the right place to optimal dispersion for active component and stabilization against sintering and gives strong impact in enhancement of cobalt FT catalyst (Wendelin et al ., 2007). Promoter are the substance that increase the catalytic activity (Chemguide., 2007).

Fourier transform infrared spectraanalysis (FTIR), N2 adsorption analysis (BET) and X-ray diffraction (XRD) were applied to analyze characterizations of the catalyst.

1.2 Problem statement

Nowadays, due to the new fuels regulation which require low sulphur content in diesel, deep hydrosulfuration is needed to remove supphur from petroleum distillates and this will drive up the cost of petroleum besed fuel. FT synthesis has become more attractive approach in producing hydrocarbon using syngas.In any industrial FT synthesis,catalyst is a vital part and one of the most important aspect during any chemical reaction.Support cobalt catalyst have been extensively used in FT synthesis when high molecular weight of hydrocarbon products is desired(Nobuntu et al ., 2005) and represent a suitable choice. Therefore, FT synthesis has become an alternative way in order to produce good and clean hydrocarbon by using syngas. In any FT synthesis for industrial application, catalyst

is the main aspect and the most important part to complete the synthesis and chemical reaction.

Then, in order to gain access to the active sites, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spillover from the promoter surface (Knifton and Lin .,1982).

So, in this research research ,we manipulated the varies of the promoter like Zirconium oxide(ZrO2),Mangan (Mn) and Zinc(Zn).The catalyst we use in this research is Cobalt(Co) and the supporter that we use is the SBA-15.We will use this three promoters to get the most efficient and increase the catalytic activity.

1.3 Objective

a) To synthesis SBA-15
b) To prepare and characterize Zr,Zn, Mn – Co based supported by SBA-15 catalysts
c) To study the activity of catalysts prepared for FT synthesis

1.4 Scope of Study

In this research, it will be focusing on the production of Co based SBA-15 catalyst by impregnation method with different loading of Zn, Mn and Zr .In this process the amount of Co is same which 20 wt % and different promoters but still the content are same which is 0.5 wt %.After that the catalyst then will be characterized by using Fourier transform infrared spectroscopy (FTIR.Then we also study the activity of different catalysts for FT synthesis to aspect the result which one the best promoters among (Zn,Mn and Zr).

CHAPTER 2

LITERATURE REVIEW

2.1 Fischer Tropsch(FT)

Fischer–Tropsch (FT) synthesis is an important catalytic process which was well-known to produce ultraclean alternative fuels from coal, natural gas and biomass via syngas . Cobalt-based catalysts have been widely applied in an FT synthesis owing to their high activity, high selectivity towards long chain *n*-paraffins, and their lower activity for the competing water gas shift reaction (WGSR). The FT synthesis activity over cobalt catalyst depended primarily on the overall amount of an exposed metallic cobalt during the reduction process, which was determined by the cobalt loading amount, metal particle size, dispersions and reduction degree. Furthermore, the chemical and texture properties of the support influenced the catalytic activity and product selectivity of cobalt catalysts via their modifications on the reducibility and dispersion of cobalt or the formation of well-fined phases. Sometimes it might be more economical to modify or change the support properties than to increase the number of active sites (Wang et al., 2011).

It has been shown that the control of hydrophilic/hydrophobic properties of supports were of importance in the preparation of catalysts and in determining the catalytic behavior. Especially, an FT synthesis is the hydrothermal reaction, because

the amount of water is produced along with the main reaction. Several researchers reported the impact of support hydrophobicity on the catalyst activity in the Fischer–Tropsch synthesis. For example(Kim and team 2007) showed that the preliminary silylation of an SBA-15 support enhanced the reducibility of the cobalt oxide species due to the weaker cobalt oxide-support interaction and consequently promoted the activity for the FT synthesis. (Ojeda et al ,. 2002) reported that the CO conversion rate increased over the silylated catalyst, because the hydrophobic surface expelled the water molecules and more surface sites were available for CO adsorption and dissociation. In our previous study found that CH_3-modified $Co/Ru/SiO_2$ catalysts showed a higher selectivity towards C_5–C_{11} hydrocarbons, which should be ascribed to its hydrophobic characteristics (Jia et al ., 2011).The figure below show the one of the reactor use in Fischer-Tropsch process.

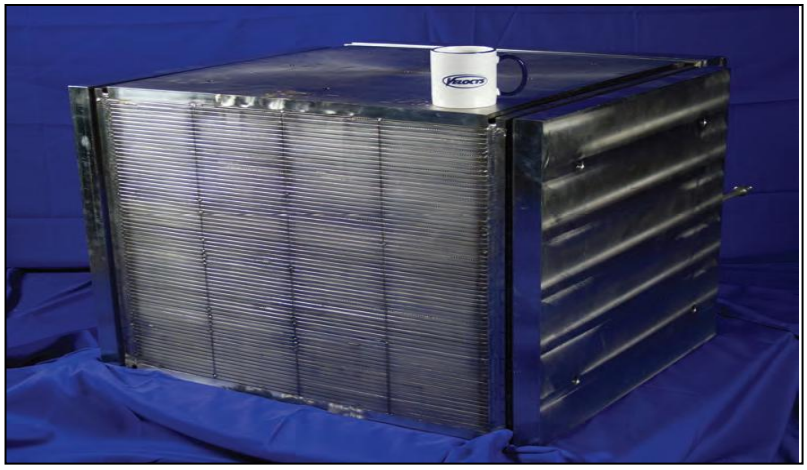

Figure 2.1: Big Daddy reactor: a full-scale microchannel Fischer-Tropsch reactor by US firm Velocys

2.2 Cobalt catalyst

Fischer–Tropsch (FT) synthesis is one major step for the transformation of nonpetroleum feedstocks, such as naturalgas, coal, and biomass, into gasoline or diesel fuel bysyngas (CO/H2). Fischer–Tropsch synthesis has received greater attention recently among scientific community and industry because of the worldwide demand for a decreased dependence on petroleum. An increasing demand for clean fuels and chemicals are expected to lead to an important shift from crude oil to natural gas as feedstock for chemical industries. This will certainly involve the use of Fischer-Tropsch (FT) technology, in which high molecular weight hydrocarbons are synthesized by catalytic hydrogenation of CO using cobalt-based FT catalysts. To date, much attention has been paid to cobalt-based catalysts Supported cobalt catalysts are well known for their activity and selectivity in the FT reaction. Optimization of cobalt dispersion and cobalt reducibility seems to be the most obvious goals in the design of efficient cobalt catalysts for FT synthesis. It has been demonstrated that catalyst preparation method, support, and promoter have important effects on the catalytic performance and structure. Strong interaction between support and cobalt species leads to high dispersion and low reducibility. A drawback of porous supports (SiO2, Al2O3) is their reactivity toward cobalt, which during preparation of catalysts results in the formation of mixed compounds such as aluminates or silicate. These cobalt-support compounds are irreversible, and it is difficult to be reduced even at 1000 K. Low degree of reduction of cobalt species on the support surface results in decreasing the number of active sites, and thus degrades the catalytic properties of the catalyst(Huang et al ., 2010).

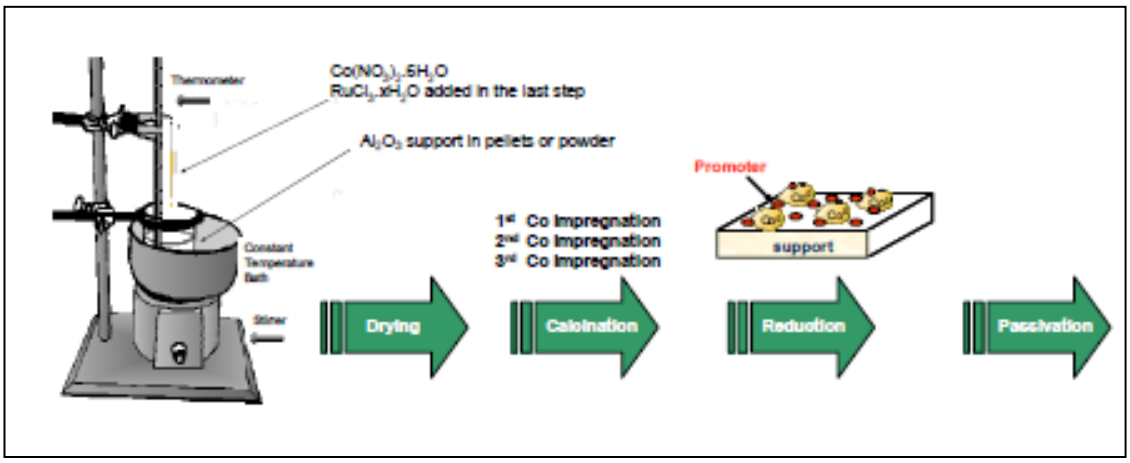

Figure 2.2: Steps preparation of catalyst

2.3 SBA-15 Supporter

The SBA-15 was many used in the recent research especially about in the Fischer-Tropsch synthesis. The recent experiment was on the Use of different mesostructured materials based on silica as cobalt supports for the Fischer–Tropsch synthesis was released by Gonza´lez and team in 2009. He published about the advantages of SBA-15 uses as cobalt supporter as saying that the use of SBA-15 as cobalt catalyst support for the FT synthesis seems to be very promising, since the Co/SBA-15 catalyst with a Dp of 5 nm has shown the best catalytic behavior in comparison with the rest of the materials tested in reaction such as Al- MCM-41 and INT-MM1.He also stated that larger surface-Co species anchored or encapsulated in the wide pore mesoporous supports showed a contrary tendency. As conclusion of his statement that SBA-15 gave more great effect on the catalyst compared with other silica such as MCM-41 and INT-MM1 in his recent research.

2.4 Promoters

These catalysts are often loaded with small amounts of promoter elements that enhance their overall catalytic performances and catalyst lifetime. These beneficial effects are, however, only obtained if the promoter element is added in the appropriate manner and in a limited range of promoter loading. Although catalyst promotion is heavily studied in the field of heterogeneous catalysis, not so much is known about the physicochemical origin of cobalt FT promotion effects. Over the past decades a large number of studies have been reported on supported cobalt FT catalysts. Generally, these studies indicate that the number of available surface cobalt metal atoms determines the catalyst activity and attempts to enhance the catalytic activity have been focusing on two interconnected issues: (1) to reduce the cobalt-support oxide interaction and (2) to enhance the number of accessible cobalt atoms available for FT reaction. It has been shown that the number of catalytically active cobalt atoms as well as their selectivity can be largely enhanced by the addition of small amounts of various elements, called promoters, to the catalyst material. However, the exact role of these promoters, as is the ase for many other heterogeneous catalysts as well, remains often unclear. The aim of this chapter is to give an extensive overview of the different promoters used to develop new or improved cobalt-based FT catalysts. Special attention is directed towards a more fundamental understanding of the effect of the different promoter elements on the catalytically active cobalt nanoparticles (Bezemer ., 2005).The goal of promotion is to enhance cobalt FT catalysts by the addition of small amounts of noble metals and metal oxides. Numerous studies have shown that introduction of a noble metal has strong impact on the structure and dispersion of cobalt species, FT reaction rates and selectivity. The promoting metal is typically introduced via co-impregnation or subsequent impregnation.

Analysis of the literature data suggests that introduction of noble metals could result in the following phenomena:

(1) Easing cobalt reduction.

(2) Enhancement of cobalt dispersion.

(3) Better resistance to deactivation.

(4) Formation of metallic alloys.

(5) High concentration of hydrogen activation site.

(6) Modification of intrinsic activity of surface sites.

2.4.1 Promoters effect

The catalyst surface often contains substances that are added deliberately to modify the turnover rate for a given catalytic reaction (Z. Paal, et al,1997). The simplest case being an additive that increases the rate per site per second. It is, in this respect, useful to recall the concepts of catalyst promotion. Promoters are doping agents added to catalyst materials in small amounts to improve their activity, selectivity and/or stability (B. Cornils ,et al,2000).

2.4.2 Structural promoters

The main function of structural promoters is to influence the cobalt dispersion by governing the cobalt-support oxide interaction (B. Cornils,et al,2000). A high Co dispersion results in a high active Co metal surface and, therefore, in a high coverage by the reactants, and as a consequence an improved catalyst activity. Structural promotion may lead to an increased catalyst activity and stability, but in principle

does not influence the product selectivity since it merely increases the number of active sites in a catalyst material. This increase in active sites can be achieved by a stabilization of the Co active phase due to the promoter element, which either avoids the formation of metal-support compounds, or prevents the agglomeration and sintering of the Co particles under F-T operation conditions.

2.4.2a Stabilizing the support oxide

Promoter elements can be added to the support oxide resulting in a decreased Co compound formation with the support oxide. This is illustrated in Figure 2.3. More specifically, strategies should be followed to avoid the formation of either cobalt titanate, cobalt silicate or cobalt aluminate as a result of Co solid-state diffusion under reducing or regeneration conditions in the subsurface of these support oxides. A related problem is the reduction in the support surface area. This is especially a problem in the case of titania, where the anatase polymorph is only stable under oxidative regeneration conditions from about 400°C to 750°C. The addition of Si, Zr and Ta as promoter elements may avoid or diminish surface collapse of the support oxide. The Figure 2.3 below show the structural promoters effect the compound formation.

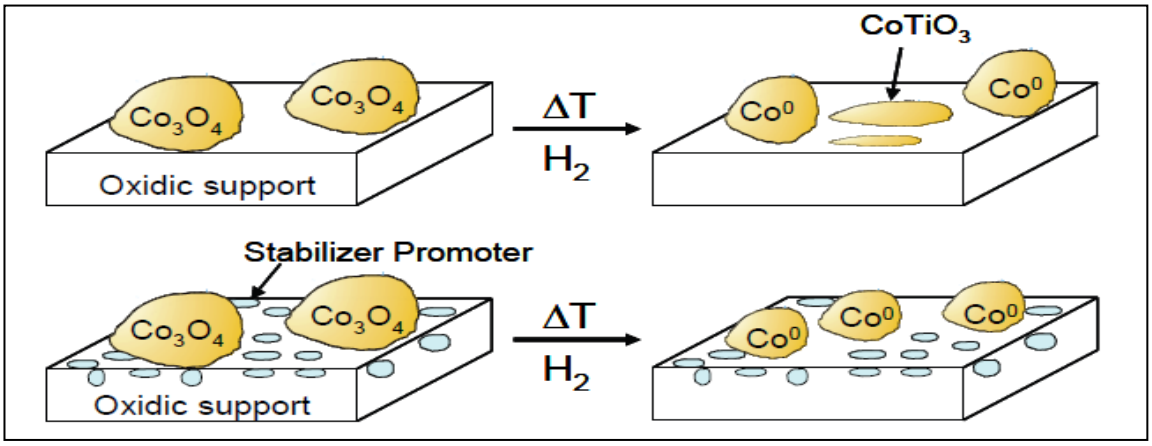

Figure 2.3: Structural promoters can lead to a decreased compound formation with the support oxide

2.4.2b Glueing the cobalt particles on the support oxide

Some promoter elements can act as an oxidic interface between the supported Co particle and the support oxide, leading to an increased stability of the cobalt particles against sintering during reduction or oxidative regeneration. A plausible schematic representation of this promotion effect is shown in Figure 2.4 below.

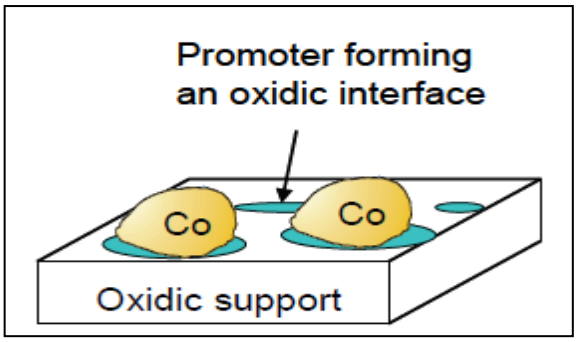

Figure 2.4: Structural promoters can act as an oxidic interface between the supported Co particle and the support oxide

2.4.2c Promoters leading to increased cobalt dispersion

The addition of promoter elements may also lead to increased cobalt dispersion after preparation. In the absence of the promoters, relatively large cobalt crystals are formed, whereas, by adding these additives, smaller supported cobalt particles can be made. Such promotion effect is illustrated in Figure 2.5 below.

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